

IV.B.1h Low-Cost Precursors to Novel Hydrogen Storage Materials

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- Innochem, Inc., Boxford, MA
- Electrolytica, Inc., Amherst, NY

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Objectives

- Overall: Develop and advance novel hydrogen storage materials to meet DOE 2010 targets and that have the potential to meet 2015 targets:
 - Leverage expertise and experience across the Chemical Hydrogen Center of Excellence (CHCoE): engineering requirements, economics, life cycle analysis.
 - Support DOE Chemical H₂ Storage Systems Analysis Sub-Group.
- Define and evaluate novel chemistries and processes for producing chemical hydrides (Phase 1):
 - Emphasize low-cost routes to regenerate sodium borohydride (NaBH₄) from spent borate fuel.
- Identify cost and energy efficient pathways to “first fill” and regeneration for ammonia borane (AB) and other borane materials (Phase 2):
 - Continue experimentation leading to selection of single pathway for low-cost NaBH₄ and further AB process technology development.
 - Guide selection of a top AB regeneration scheme for experimental studies on most promising alternatives.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) System Cost
- (C) Efficiency
- (K) System Life-Cycle Assessments
- (R) Regeneration Processes

Technical Targets

- **Fuel Cost and Energy Efficiency (NaBH₄ as Fuel)** – Table 1 shows progress against meeting the DOE 2010 targets for fuel cost and energy efficiency using two potential routes to regenerate sodium borohydride from sodium metaborate: metal reduction and carbothermal reduction.

TABLE 1. Progress Towards Meeting DOE Targets for NaBH₄ Fuel Cost and Energy Efficiency

	Fuel Cost, \$/kg H ₂	Fuel Efficiency ^a
DOE 2010/2015 Target	2 - 3	60%
Metal Reduction	6 - 12	19% (43%)
Carbothermal Reduction	2 - 7	19% (50%)

^a Values in parentheses represent use of hydroelectric power as electricity source

Although our analyses show that it will be difficult to meet the DOE hydrogen cost and efficiency targets with either of these improved routes, they have the potential to yield significantly lower cost NaBH₄ than is possible with the current commercial process. Since NaBH₄ is the dominant raw material cost in the synthesis of AB and other borane-based on-board H₂ storage systems under consideration, improvements in its production cost will lead to substantial cost benefits for these systems.

- **Storage System Cost (Ammonia Borane as Fuel)** – Table 2 shows preliminary estimates for AB cost (\$/kg) produced from NaBH₄ using the metal reduction and carbothermal routes. Target AB costs were calculated from DOE cost targets and assuming the AB media is 33% of the storage system cost.

TABLE 2. Progress Towards Meeting DOE Storage System Cost Target for Ammonia Borane

	Storage System Cost, \$/kg H ₂	AB Cost, \$/kg ^b
DOE 2010 Target	133	5.8
DOE 2015 Target	67	2.9
Metal Reduction		1.6 – 3.1
Carbothermal Reduction		0.5 – 1.8

^b Assumes media is 33% of storage system cost

These results indicate that with either NaBH₄ pathway, the AB media cost can be reduced to having a minor contribution to the total system cost.

Accomplishments

- Identified feasibility of two new low-cost NaBH₄ routes: metal reduction of borate and carbothermal reduction of borate.
- Demonstrated key chemistry step of NaBH₄ formation for the top pathways.
- Developed conceptual processes that show significantly improved energy efficiency and lower cost compared to current Schlesinger technology.
- Terminated support of research on electrochemical borate reduction pathways at Penn State.
- Initiated analysis support to spent AB regeneration efforts.



Introduction

This project focuses on identifying and developing viable hydrogen storage technologies using chemical hydrides that have the potential to achieve DOE 2010 and 2015 performance targets for transportation applications. In collaboration with the other CHCoE participants, efforts are directed towards defining and evaluating novel chemistries and processes for producing chemical hydrides. In Phase 1, emphasis was on NaBH₄, initially a strong candidate for hydrogen storage because of its hydrogen storage capacity, chemistry, safety, and functionality.

The ability to produce low-cost NaBH₄ in an energy-efficient, cost-effective, and environmentally sound manner is critical to the commercial success of virtually any boron-based fuel, including AB. In Phase 2, research will continue towards identifying and developing a single low-cost NaBH₄ synthetic route for cost-efficient AB first fill.

Approach

This project utilizes an engineering-guided research and development (R&D) approach. This entails the rapid down-selection of a large number of options (pathways to NaBH₄) to a smaller, more manageable number of options. The down-selection is based on evaluation against a set of established metrics and occurs to a large extent before any experimentation is initiated.

The overall process involves 1) identifying leading pathways, 2) determining the feasibility of the leading pathways, 3) detailing performance to select a single, top pathway, and 4) developing the single, top pathway. As one progresses through the process, more accurate and detailed process and economic analyses are realized. This approach serves to focus efforts and resources on those options that have the highest technical and commercial probability of success.

Results

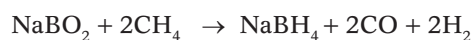
Previously, we reported on the selection of metal reduction and carbothermal reduction as the two leading pathways to convert borate to borohydride, based on a comprehensive review of possible pathways and scoring against established metrics.

Metal borate reduction can proceed via a one-step or two-step process, as shown below:

- 1-step: $\text{NaBO}_2 + 2x/y \text{ M} + 2\text{H}_2 \rightarrow \text{NaBH}_4 + 2/y \text{ M}_x\text{O}_y$
- 2-step: $2x/y \text{ M} + 2\text{H}_2 \rightarrow 2x/y \text{ MH}_{2y/x}$
 $\text{NaBO}_2 + 2x/y \text{ MH}_{2y/x} \rightarrow \text{NaBH}_4 + 2/y \text{ M}_x\text{O}_y$

Generally, this approach enables the use of lower-cost metals than sodium, and with more efficient utilization. The current Schlesinger process suffers from poor Na utilization (4 mols Na metal to produce 1 mol NaBH₄). Recycle of the resulting metal oxide back to the metal in a cost-effective manner is also required. Reactive milling techniques are an important consideration with this chemistry.

Carbothermal borate reduction is characterized by the equation below:



Methane instead of metal is used as the reductant, thereby eliminating the need for metal oxide recycle and associated cost and energy requirements. High temperatures (generally >1,000°C) are required before these reactions become thermodynamically favorable (negative Gibbs free energy). Syngas (CO/H₂), a commercially viable product, is produced.

Studies on both one- and two-step metal reduction systems have progressed in-house using different reactor configurations and a variety of metals (Mg, Al, Ti, Si,

and Zn), milling media, and conditions (milling severity, milling time). Borohydride yields of 100% have been achieved in some instances, as confirmed by ¹¹B nuclear magnetic resonance (NMR).

Carbothermal reduction of borate to borohydride, using plasma techniques, has been under investigation at Idaho National Laboratory (INL). Figure 1 is a

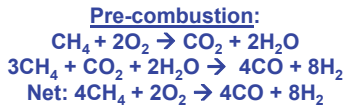
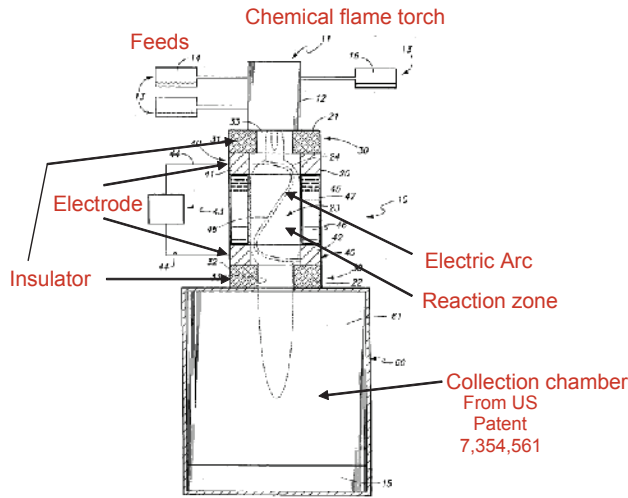


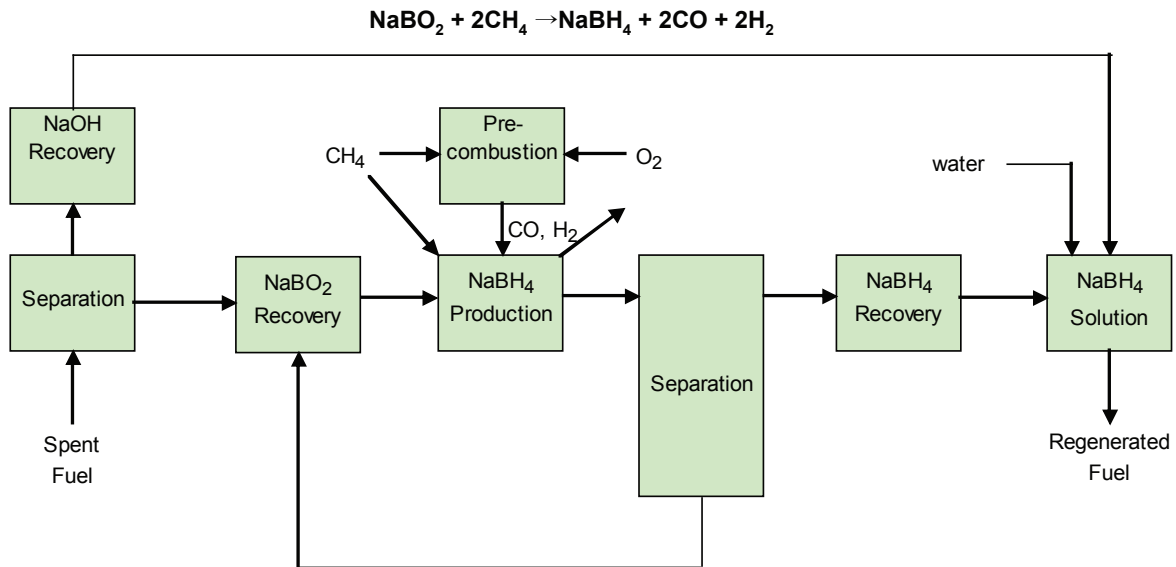
FIGURE 1. Plasma Carbothermal Reduction of Borate to Borohydride (Idaho National Laboratory)

schematic of one of INL’s reactor configurations. The process begins with a combustion flame, across which an electric arc is applied, resulting in a high-temperature plasma. INL has reported borohydride yields in the range of 40–50% in a one-step reduction, also confirmed by ¹¹B NMR analysis. Operating conditions have not yet been optimized.

Once the key chemistry step(s) of borohydride formation was demonstrated, conceptual process flowsheets were developed for both the metal reduction and carbothermal reduction routes. Figure 2 shows the conceptual process for carbothermal reduction. Starting with the conceptual process flowsheets, and using experimental data (yields, reaction conditions), a detailed analysis of these conceptual processes was conducted to arrive at preliminary overall process efficiencies and delivered hydrogen costs. A variety of tools was used, including H2A, FCHTool, and Aspen IPE™ to arrive at raw material, energy, utility, labor/maintenance, capital, overhead, and maintenance costs. Figure 3 illustrates the overall methodology used in this process.

Using this methodology, overall process efficiencies of 43% and 50% were obtained for the metal reduction and carbothermal routes, respectively, assuming the use of hydroelectric power as the source of electricity. Efficiency drops to 19% if the 2015 US electric grid is applied. In either case, the efficiencies do not meet the DOE target of 60%.

Delivered hydrogen costs for metal reduction and carbothermal routes, were calculated to be \$6-12/kg H₂ and \$2-7/kg H₂, respectively. Sensitivity analyses were conducted to determine various parametric effects on



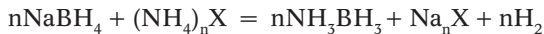
Lower cost and higher efficiency process expected with elimination of metal recovery.

FIGURE 2. NaBH₄ Regeneration Conceptual Process Using Carbothermal Reduction

cost. Figure 4 shows the sensitivity analysis for the carbothermal process. With favorable electricity pricing from hydroelectric power and credit for syngas production, these would be on a good trajectory toward achieving the DOE fuel target cost of \$2-3/kg H₂.

Despite good progress toward achieving the fuel cost target, in November 2007 an independent review panel issued a No-Go decision for sodium borohydride for on-board hydrogen storage and release. This is principally because of difficulties achieving the capacity performance targets due to solubility issues associated with the spent fuel, and in part because of the inability to meet the 60% efficiency target. However, the review panel recommended that research activities on low-cost NaBH₄ routes continue. This is because NaBH₄ is a key starting material for AB and other borane- and boron-based on-board H₂ storage systems under consideration, including many selected by the Metal Hydride Center of Excellence as showing promise as a viable hydrogen storage material.

NaBH₄ is a dominant component of the cost to produce AB:



Technologies to produce NaBH₄ at lower cost are critical with respect to meeting ammonia borane first fill system cost requirements. Our preliminary delivered

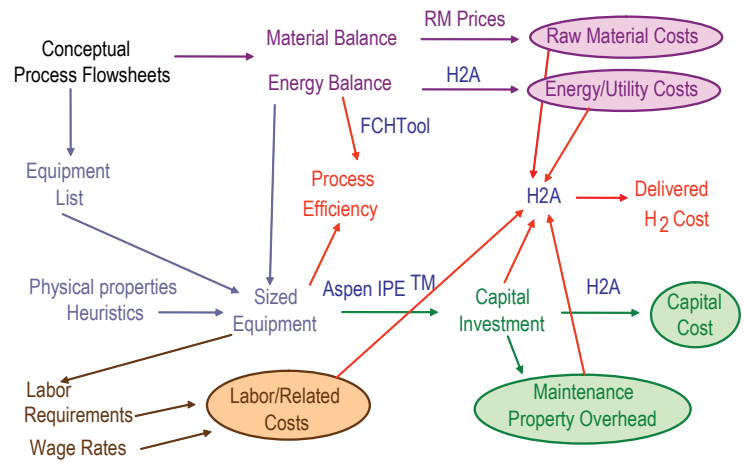


FIGURE 3. Cost Estimating Methodology for Conceptual Process

hydrogen costs for metal reduction and carbothermal routes indicate that first fill system cost targets will likely be met for 2010, and possibly 2105, for AB produced from NaBH₄ by these routes.

Finally, we continued to collaborate with Penn State on electrochemical studies for both one-step reductions in aqueous media as well as reductions in non-aqueous systems, using a variety of high hydrogen potential cathode materials. NaBH₄ production has been demonstrated, but poor yields and irreproducibility of the data caused this project to be terminated. Details can be found in Penn State’s Annual Report.

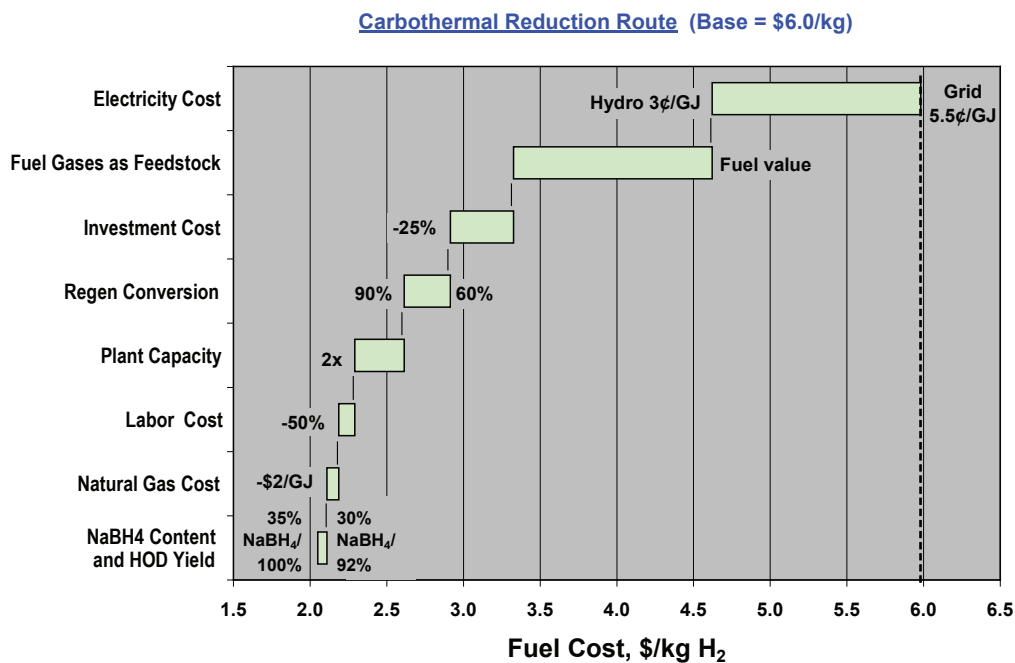


FIGURE 4. Sensitivity Analysis for Delivered Hydrogen Cost (Carbothermal Process)

Conclusions and Future Directions

Conclusions

- Experimental studies confirmed feasibility of two leading pathways for regenerating NaBH_4 from spent borate fuel, metal reduction and carbothermal reduction:
 - Both show potential for significant cost improvement over current Schlesinger process.
- Independent review panel found the chemistry to be sound, but at an early stage. NaBH_4 analysis methodology were found to be very valuable and applicable to AB and other promising storage materials.
- Research on low-cost pathways to NaBH_4 will continue, since NaBH_4 is a key starting material for AB and other borane-based materials under consideration:
 - Improvements in NaBH_4 production will lead to cost-effective “first fill” for these systems.
- Phase 2 focus will involve detailing conceptual process and cost for top NaBH_4 pathway and applying metrics-based NaBH_4 pathway analysis to AB assessments.

Future Directions

- Progress process R&D to create high-yield, low-cost scalable NaBH_4 process for first fill AB:
 - Continue studies on both metal-based and carbothermal reduction.
 - Select single top pathway.
- Support AB synthesis and regeneration research:
 - Apply NaBH_4 metrics-based process to select top AB pathways.
 - Provide conceptual process development and cost estimates.
 - Conduct “first fill” AB synthesis process analysis.
- Leverage Rohm and Haas competencies across the CHCoE:
 - Process development.
 - Engineering assessment.

Awards/Patents Issued

1. Process for production of a borohydride compound, US 7297316, A. A. Chin, November 20, 2007 (granted as background IP).
2. Preparation of boron and sodium by sodium metaborate reduction for the synthesis of sodium borohydride, EP 1645644 B1, Chin et al, December 26, 2007 (granted as background IP).

FY 2008 Publications/Presentations

1. F. Lipiecki, A. Chin, L. Klawiter, and S. Linehan, “DOE Review Panel Meeting for Go/No Go Decision on NaBH_4 Hydrolysis for On-Board H_2 Storage – Sodium Borohydride Regeneration”, presentation for Go/No Go Review, Argonne, IL, September 11, 2007.
2. L. Klawiter, F. Lipiecki, A. Chin, “Cost Estimating Methodology for Regenerating NaBH_4 ”, SSAWG Meeting, Washington, DC, December 4, 2007.
3. C. Aardahl, S. Linehan, F. Lipiecki, A. Chin, L. Klawiter, S. Rassat, R. Zheng, T. Semelsberger, O. Moreno, “Engineering Developments within the Chemical Storage COE: On-board & Off-board Issues”, US FreedomCar Tech Team Meeting, Dearborn, MI, January 17, 2008.
4. S. W. Linehan, F. J. Lipiecki, A. A. Chin, and L. Klawiter, “Low-Cost Precursors to Novel Hydrogen Storage Materials”, DOE Annual Merit Review, Washington, D.C., June 10, 2008.